



RESEARCH MEMORANDUM

EFFECTS OF MOLECULAR WEIGHT ON CRAZING AND TENSILE
PROPERTIES OF POLYMETHYL METHACRYLATE

By I. Wolock, M. A. Sherman, and B. M. Axilrod

National Bureau of Standards

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Page 11, the key label in figure 2 should read:

—————Ultimate elongation

-----Strain at onset of crazing

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SUMMARY

Tensile and crazing properties are reported for five cast polymethylmethacrylate sheets in which the molecular weight of the resin was 90,000, 120,000, 200,000, 490,000, and 3,160,000, respectively. Both stress crazing and stress-solvent crazing tests were conducted. It was found that the tensile strength and ultimate elongation increase rapidly with increasing molecular weight at the lower molecular weights and begin to level off at molecular weights of approximately 200,000 and 500,000, respectively. There was no change in the modulus of elasticity over the range of molecular weights studied. The specimens with lowest molecular weights broke at low strains without crazing. For the higher molecular weights, the stress and the strain at which crazing occurred increased with increasing molecular weights. In the stress-solvent crazing tests, the lower molecular weight materials broke immediately upon crazing, usually at an observed craze crack. For the two highest molecular weights there was a slight indication of increased craze resistance with increase in molecular weight.

INTRODUCTION

The molecular weight of a high polymer has a marked effect on its mechanical properties (refs. 1 to 5). Properties such as tensile strength increase roughly in direct proportion to the molecular weight up to a certain point, after which the tensile strength starts to level off and becomes fairly constant.

Crazing of polymethyl methacrylate has been associated with the initiation of tensile failure (ref. 6). In view of the dependence of tensile strength on molecular weight, this investigation was undertaken to study the effects of molecular weight on the crazing of polymethyl methacrylate.

This investigation was conducted at the National Bureau of Standards under the sponsorship and with the financial assistance of the National

Advisory Committee for Aeronautics. The authors gratefully acknowledge the courtesy of Professor A. G. H. Dietz of the Massachusetts Institute of Technology in supplying the materials used in this investigation and the assistance of Messrs. John W. McElwain and S. Rothman of NBS in checking the solution viscosities of the test materials.

MATERIALS

The materials studied, supplied by Professor A. G. H. Dietz, were specially cast polymethyl-methacrylate sheets prepared by the Rohm & Haas Co., Inc., in five different average molecular weights. The materials were reported to contain small amounts of catalyst and parting agent and were reported to be as monodisperse as possible (ref. 3). The sheets received were approximately 1/4 inch thick and 12 inches square. The viscosity average molecular weights of the five materials were 90,000, 120,000, 200,000, 490,000, and 3,160,000.

Specimens were tested from two sheets of each of the five molecular weights. One set of samples, consisting of one sheet of each of the five materials, was tested at one time and another set of five sheets received at a later date was tested 5 months later. The respective sheets in the two sets were reported to have been cast from the same monomer solutions.

TEST PROCEDURE

Standard tensile and stress-solvent crazing tensile tests were made at $23^{\circ} \pm 1^{\circ}$ C and 50 ± 2 percent relative humidity, using a 2,400-pound-capacity Baldwin-Southwark universal hydraulic testing machine.

Standard Tensile Tests

The standard tensile specimens were those of type I of Method 1011 of Federal Specification L-P-406b. The tests were conducted according to Method 1011, the relative rate of head motion being 0.05 inch per minute. Four specimens were tested from each sheet of each sample. Load-elongation graphs were obtained by means of a strain gage and the associated autographic recorder. The strain gage used was a model PS-6 Southwark-Peters plastics extensometer, a high-magnification nonaveraging type with a 2-inch gage length and a strain range of 10 percent. On the first set of tests, the gage operated with an electric contact-type stress-strain recorder. When the second set of tests was made, the strain gage was modified to operate with a microformer-type stress-strain recorder.

The modified gage was somewhat heavier than the original gage. The threshold of stress crazing was observed visually and marked on the load-elongation graph. A fluorescent lamp was so placed behind the specimen as to make the crazing easily seen as it appeared.

Stress-Solvent Crazing Tests

The stress-solvent crazing tests were made using tensile specimens with a 3-inch-long reduced section tapering uniformly in width from 0.50 inch at the maximum cross section to 0.33 inch at the minimum. Thus, for a given applied load, the stress varied along the length of the specimen from S at the minimum cross section to $\frac{2}{3}S$ at the maximum. In this way, the minimum stress required to cause crazing could be determined with one specimen. The stress that might be expected to be the threshold of stress-solvent crazing for the material was estimated from earlier results. A load was then applied to the specimen such that this stress would be reached near the middle of the specimen. This load was held constant while solvent was applied and for about 2 minutes thereafter.

In the first set of tests, the solvent was applied by holding a solvent-saturated blotter ($3/16$ inch by 3 inches), backed with a block of polyethylene, against one face of the specimen for 10 seconds. The solvent used in these tests was benzene. Two or three specimens of each of the materials in the first shipment were given stress-solvent tests. Since so many of the specimens broke in these tests, the test method was modified for the second set of specimens in an effort to make the solvent treatment less drastic. This was attempted by using a brush for the application of solvent instead of a blotter, and by using isopropanol instead of benzene. In the brush method 0.03 to 0.04 cubic centimeters of solvent was applied to a No. 1 camel's hair brush from a graduated glass dropper. The central $1/4$ - by 3-inch portion of the specimen was then stroked with the brush until the latter was dry. The test method used in the first set of tests was repeated in the second set for comparison. From the second set of materials, therefore, four specimens from each sample were tested with each of two solvents, benzene and isopropanol, applied by brush on two specimens and by blotter on the other two. In each case, the crazing threshold was taken as the stress at the point below which there were no visible craze cracks.

RESULTS AND DISCUSSION

Standard Tensile Tests

The results of the standard tensile tests are shown in table I. Average values are presented for each of the five samples for each of the

two sets of tests. The tensile strength and threshold crazing stress are shown graphically in figure 1 and the ultimate elongation and threshold crazing strain, in figure 2. The range of molecular weights of commercial cast polymethyl methacrylate is indicated in these figures.

In both sets of tests the tensile strength increased rapidly with increasing molecular weight up to a molecular weight of approximately 200,000, at which point the tensile strength began to level off and increased only a few percent for the higher molecular weights. The total elongation also increased rapidly with increasing molecular weight in the lower molecular weights and began to level off at a molecular weight of approximately 500,000, increasing only slightly for the higher molecular weights. The values obtained for the secant modulus of elasticity were fairly constant at approximately 4.2×10^5 psi over the range of molecular weights studied.

Both the stress and the strain at which crazing occurred in the standard tensile tests also increased with increasing molecular weight. In the first group of tests, however, the specimens of the lowest molecular weight material broke at low strains with no visible craze cracks, and, in the second group of tests, the samples in the two lowest molecular weights broke with no crazing observed.

The results obtained in the two sets of tests agreed qualitatively in regard to the influence of molecular weight on the properties, as shown in figures 1 and 2. However, the values obtained for tensile strength and total elongation in the first set were consistently higher than those for the corresponding materials in the second set; moreover, the differences between corresponding values were significant for the two materials of lowest molecular weight. In contrast to the tensile strength and elongation data, the threshold crazing stress and strain values for the first set of samples were consistently and usually significantly lower than for the second set. These differences between the values for the two sets of data could be due to differences in molecular weight of corresponding materials in the two sets, but this explanation seems unlikely since the two sheets of each material were cast from the same batch of monomer at the same time. The solution viscosity of each material was checked at this laboratory and there was no significant difference in the viscosities of corresponding materials in the two sets. In addition, the differences observed in the two sets of data were consistent and variations in molecular weight in the five materials probably would not result in such consistency.

The lower values for tensile strength and ultimate elongation in the second set of tests may be due to the modified strain gage, which was heavier than the one used in the first set of tests and applied a greater bending moment to the specimens. Also, the knife edges of the gage had been sharpened when the gage was modified. These changes could lead to

earlier rupture of the specimens. This would not, however, account for the differences in the values obtained for the crazing properties. These differences may be due at least in part to the fact that the onset of crazing is observed visually, and the two sets were tested by two different persons.

The values for modulus of elasticity, which should not be affected by either the heavier strain gage or the operator, were quite similar for both sets of tests as shown in table I. The stress-strain diagrams did not vary significantly with molecular weight except for the rupture point. A similar result was noted for polymethyl methacrylate films by Hauser and Patterson (ref. 7). As Maxwell points out (ref. 8), the slope of the initial portion of the load-deformation curve depends on the force required to bend the bond angles of the polymer chains. The bond angle is a property of the molecule and the force required to bend this angle should not be a function of the molecular weight. Thus the values for modulus of elasticity should not vary significantly with molecular weight.

Stress-Solvent Crazing Tests

In the stress-solvent crazing tests, the low-molecular-weight samples did not exhibit crazing behavior similar to that previously observed in commercial cast polymethyl methacrylate. In the case of the commercial materials, as well as in the case of the two highest molecular weight materials, upon the application of solvent to the surface of a tapered specimen under load the specimens would craze from the minimum width down to a cross section corresponding to the threshold stress for stress solvent crazing. For the samples of the three lowest molecular weights, 90,000, 120,000, and 200,000, however, a load sufficiently high to cause crazing upon the application of solvent also caused failure. A few long craze cracks would develop and the specimen would fail almost immediately, usually at an observed craze crack at or near the minimum cross section. The minimum loads at which these specimens broke varied from 1,400 to 1,900 psi with a tendency for the lowest molecular weight specimens to fail at the lower loads.

Several of the low-molecular-weight specimens were observed from the front by one person and from the side by another when solvent was applied. A craze crack was observed to form at or near the minimum width and then propagate rapidly through the thickness of the specimen in two or three spurts in a plane perpendicular to the faces of the specimen. This resulted in immediate failure of the specimen. The fracture surfaces contained a mirrorlike area always adjacent to the surface of the specimen to which solvent had been applied. It was postulated in a previous report (ref. 6) that this area was the extension of a craze crack and was the origin of failure. The observations made on these low-molecular-weight specimens tend to substantiate this postulate.

For the materials having the highest molecular weights (490,000 and 3,160,000), the small number of specimens tested did not indicate any significant difference in threshold-stress values for the two methods of solvent application (brush and blotter) or for the two solvents used (benzene and isopropanol). There was a slight indication of higher craze resistance for the higher molecular weight material. The average values obtained for the threshold crazing stress, combining the results obtained by the two methods and for the two solvents, were 2,700 psi for the 490,000-molecular-weight and 2,850 psi for the 3,160,000-molecular-weight material.

Discussion of Failure and Crazing

A qualitative explanation has been offered for the dependence of tensile strength on molecular weight (refs. 3 and 4). Apparently in a polymer of low molecular weight, the forces required to cause adjacent chains to slide relative to one another are relatively weak because of the short length of the chains and subsequent small number of secondary valence linkages. As a result, failure occurs by the rupture of secondary valences at chain ends rather than by the rupture of primary valence bonds. As the molecular weight increases, the resistance to sliding of adjacent chains increases to the extent that it becomes easier to cause rupture by the breaking of primary valence bonds than for the larger chains to slide past one another. Thus, the mechanical properties show a marked dependence on chain length or molecular weight.

The phenomena of crazing and of fracture are believed to be closely related as suggested previously (ref. 6). In polymeric materials which exhibit crazing, the latter phenomenon may be looked on as an initial phase of the fracture process. In the present experiments, however, it is interesting to note that in the standard tensile tests the lowest molecular weight materials broke at low strains with no visible crazing. One possible explanation of the latter behavior is as follows.

In a theory proposed previously (ref. 6) crazing originates in submicroscopic regions in which the polymer chain segments are oriented perpendicularly to the direction of the applied tensile load line. The macromolecules are pictured as roughly spherical in shape and closely packed. A submicroscopic crack starts by separation of segments of adjacent chains and, because of stress concentration, grows quickly until it reaches a region in which the polymer chain segments are oriented predominantly parallel to the applied load. This region either halts or slows the crack growth. In the case of polymers of low molecular weights, assuming the same picture of initiation of a crack, the following behavior is postulated. When the submicroscopic crack reaches a region in which the segments of adjacent chains are oriented approximately parallel to the tensile load line, the total secondary forces resisting shearing or

sliding separation of the adjacent chains are too small to prevent sliding; thus crack propagation is not impeded. This process then proceeds rapidly to failure and no crazing is observed. As the molecular weight is increased the total secondary forces between chains become greater so that at some point the growth of the crazing crack is impeded when it reaches the region in which the chain segments are oriented approximately parallel to the tensile load line.

The relatively brittle nature of the low-molecular-weight materials was shown in the stress-solvent crazing tests. In these tests, specimens of the three materials with lowest molecular weights always ruptured immediately upon crazing.

SUMMARY OF RESULTS

An investigation of the tensile and crazing properties of polymethyl methacrylate of molecular weight ranging from 90,000 to 3,160,000 indicated the following dependence on molecular weight:

1. The tensile strength and ultimate elongation increase rapidly with increasing molecular weight at the lower molecular weights and start to level off at the higher molecular weights. The modulus of elasticity does not vary over the range of molecular weights studied.
2. The materials with lowest molecular weights break at low strains with no crazing observed. For the materials with higher molecular weights, the stress and the strain at which crazing occurs in short-time tensile tests increases slightly with increasing molecular weight.
3. In the stress-solvent crazing tests, the materials with lowest molecular weights break immediately upon crazing. The craze resistance increases slightly with increasing molecular weight at the higher molecular weights.

National Bureau of Standards,
Washington, D. C., February 20, 1953.

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TABLE I.- EFFECT OF MOLECULAR WEIGHT ON TENSILE PROPERTIES OF POLYMETHYL METHACRYLATE

[Average of four specimens, unless otherwise noted, plus or minus standard error]

| NBS sample number | Sheet number | Viscosity molecular weight | Tensile strength, psi | Total elongation, percent | Stress at onset of crazing, psi | Strain at onset of crazing, percent | Secant modulus, psi (a) |
|-------------------|--------------|----------------------------|--------------------------|---------------------------|---------------------------------|-------------------------------------|-------------------------|
| First set | | | | | | | |
| PM-1 | B279-1 | 90,000 | 6,600 ± 180 | 1.8 ± 0.1 | (b) | (b) | 4.3 ± 0.1 |
| PM-2 | B281-1 | 120,000 | ^c 8,500 ± 620 | ^c 2.8 ± 0.4 | ^d 7,860 ± 160 | ^d 2.3 ± 0.1 | 4.2 ± 0.1 |
| PM-3 | B284-1 | 200,000 | 10,050 ± 120 | 4.7 ± 0.4 | 8,320 ± 150 | 2.6 ± 0.1 | 4.2 ± 0.1 |
| PM-4 | B285-1 | 490,000 | (e) | (e) | (e) | (e) | (e) |
| PM-5 | B287-1 | 3,160,000 | 10,200 ± 120 | ^f >7.2 ± 1.4 | 8,750 ± 60 | 3.0 ± 0.0 | 4.1 ± 0.1 |
| Second set | | | | | | | |
| PM-1 | 279-5 | 90,000 | ^g 5,410 ± 180 | ^g 1.3 ± 0.0 | (b) | (b) | 4.3 ± 0.1 |
| PM-2 | 281-5 | 120,000 | 6,860 ± 140 | 1.9 ± 0.1 | (b) | (b) | 4.2 ± 0.1 |
| PM-3 | 284-5 | 200,000 | 9,720 ± 150 | 4.3 ± 0.3 | 9,130 ± 70 | 3.5 ± 0.2 | 4.2 ± 0.1 |
| PM-4 | 285-5 | 490,000 | ^h 9,980 ± 120 | ^h 5.8 ± 1.1 | ^h 9,330 ± 430 | ^h 3.7 ± 0.5 | 4.2 ± 0.1 |
| PM-5 | 287-5 | 3,160,000 | 10,180 ± 130 | 6.0 ± 0.7 | 9,750 ± 100 | 4.0 ± 0.1 | 4.3 ± 0.2 |

^aStress range used for calculation of secant modulus was 0 to 4,000 psi.^bAll specimens broke before crazing.^cAverage of three specimens. One specimen broke prematurely in grips.^dAverage of two specimens. One specimen broke prematurely in grips; one specimen broke without crazing.^eAll specimens broke prematurely at bubbles present in this sheet.^fOne specimen elongated more than 10 percent, the maximum indicated by strain gage.^gAverage for three specimens; one specimen failed prematurely at a scratch.^hAverage for two specimens; two specimens broke prematurely in grips before crazing.

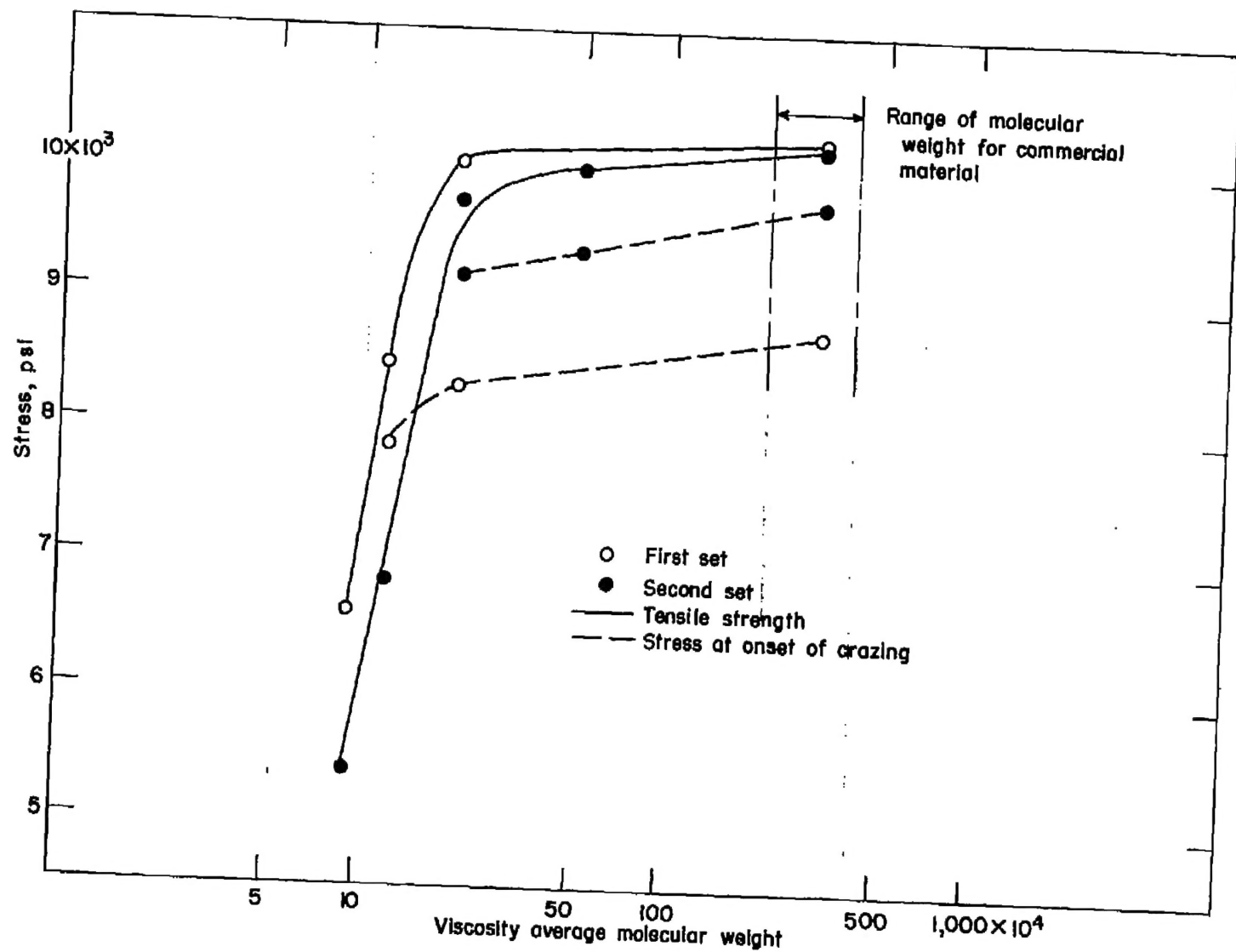


Figure 1.- Variation of tensile stress with molecular weight.

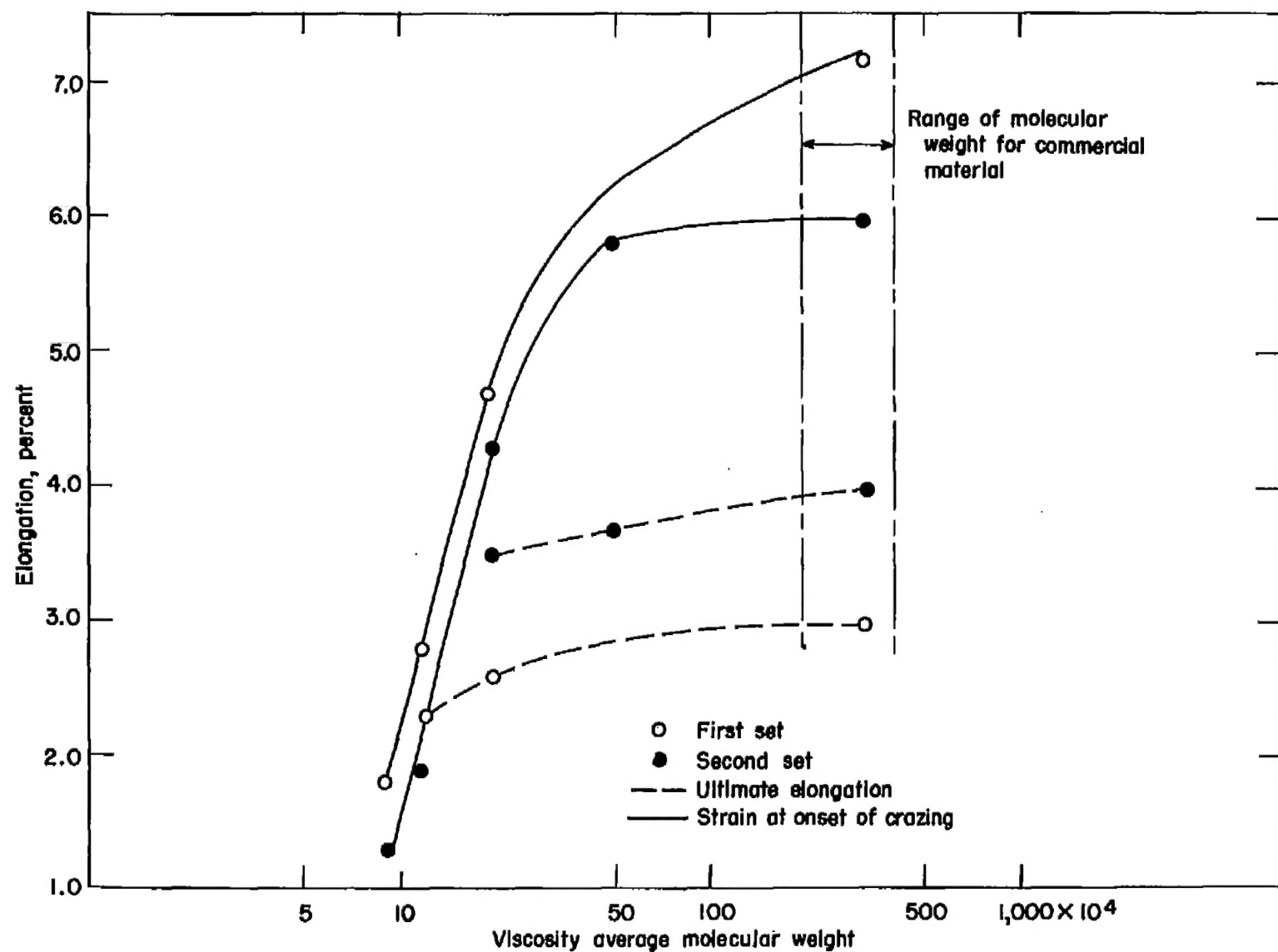


Figure 2.- Variation of elongation with molecular weight.